Synthetic Organic Chemicals

PUBLISHED BY THE

EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

VOL. IV PUBLISHED DECEMBER, 1930 NO. 2

Reference Fuels Used as Anti-Knock Standards

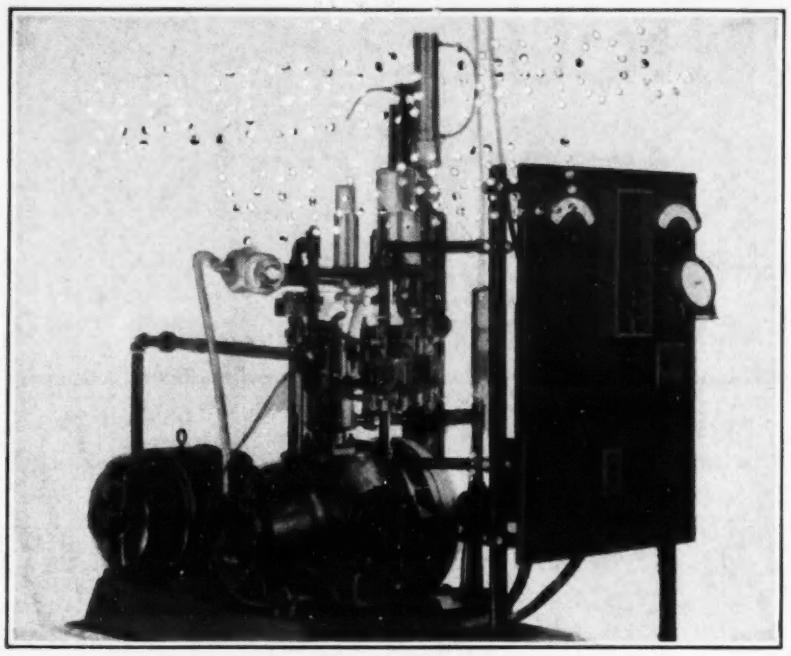
THE widespread use of gasolines "doctored" to give a motor fuel that will not knock, and the recent design of automobile engines to make the most efficient use of the gasolines, requires a standard method for evaluating the various fuels. Knocking is the characteristic "ping" noticed when a gasoline engine is laboring at full load or when the cylinders are badly carbonized. It is an indication that the combustion of gasoline vapor is taking place too rapidly to give the maximum energy to the piston.

The more closely the vapor is compressed, the greater is the tendency to knock. A high compression engine, in which the volume of the vapor is compressed in the ratio of 6 to 1, will thus knock more readily than one in which the volume change is only 5 to 1. In addition to the increased thermal efficiency there is an advantage in having the compression ratio of a motor as high as practicable, since the piston will have a greater displacement on the down stroke, thus increasing the power.

The relationship between knocking tendency and compression has led to the development of several methods for comparing fuels. Specially built one-cylinder engines are in use in which the compression ratio can be varied while running, by moving the entire cylinder-head up and down. The change in position of the cylinder-head is measured by a micrometer from which the actual compression ratio can be calculated. All other conditions, including temperature, spark advance, fuel input, load and speed, are kept constant. In testing a fuel the air inlet is adjusted to give a mixture of maximum power as indicated by the dynamometer coupled to the shaft. The compression ratio is then gradually increased by moving the cylinder head to the point where the first audible knock is heard.

Instead of using the variable compression-ratio engine described, a fixed compression-ratio motor may be used and the actual pressures changed by varying the throttle position. The illustration on the next page shows a testing engine used by the Engineering Laboratories of the Ethyl Gasoline Corporation. Various mechanical devices have also been designed to eliminate personal variances in detecting the first audible knock. Since there are many variable factors, the actual readings on different motors will not be identical. If, however, two fuels are examined with the same engine, under the same conditions, the comparative results will be similar to those obtained on other engines. For correlation, it is only necessary to have a standard fuel in terms of which all others can be compared.

Gasolines vary widely in their composition, depending on their source and method of refining. It would be very difficult to find a suitable reproducible



A fixed compression-ratio testing engine

gasoline that would approach the uniformity of a chemical compound. Normal heptane is a constituent of many gasolines, and, since it can be prepared in a pure form, is widely accepted as a primary standard in anti-knock investigations. The knocking tendency of any fuel can be evaluated against it by comparing the compression ratios at which knocking begins. Heptane also has the advantage that, while it knocks at very low compression ratios when used alone, it can be mixed with other pure hydrocarbons to give fuels with a wide range of knocking characteristics.

The hydrocarbons which have shown the most promise as standards for reducing the knocking of heptane are benzene, cyclohexane, iso-octane, and toluene. Any one of the four can be mixed with normal heptane in such a proportion as to match identically the knocking qualities of the gasolines used as fuel today.

Benzene and toluene have been favored in Great Britain, and several laboratories there report the knock rating of gasolines in terms of the percentage of pure benzene in heptane. A good grade of anti-knock gasoline has a benzene value of 65 which means that it corresponds in behavior to a mixture of 65%, by volume, of benzene in heptane. One disadvantage in the use of benzene is that at the higher values a small change in the benzene percentage makes a large change in the knock value so that the mixture must be made up very accurately. Also benzene and normal heptane differ somewhat in physical characteristics.

The continuous addition of cyclohexane to heptane varies the knocking properties quite evenly throughout its range. Unfortunately, however, pure cyclohexane itself knocks at moderately high compression ratios so that its use is necessarily limited.

Since iso-octane (2.2.4-trimethyl pentane) has marked anti-knock characteristics, it can be mixed with heptane to give a series of standards extending beyond the present range of automobile fuels. Its chemical structure is more closely allied to heptane than are the other hydrocarbons, and its density and boiling point are almost identical with those of normal heptane. Several of the laboratories in this country are standardizing on heptane-iso-octane percentages for rating anti-knock fuels. A 71% iso-octane rating is approximately equivalent to 65% benzene. Owing to the high cost of the pure heptane and iso-octane, they are used principally as primary standards.

The actual comparisons of commercial fuels are carried out in the laboratories against a selected lot of gasoline. The pure hydrocarbons are used to standardize this gasoline and to check the uniformity of operation of the test motor. Modifications of the methods described have been suggested and several ingenious devices are being used to determine the point of incipient knocking more accurately than by the human ear. All of the methods, however, require a standard fuel for reference. It is quite likely that international standards for anti-knock measurements will be chosen from the hydrocarbons mentioned.

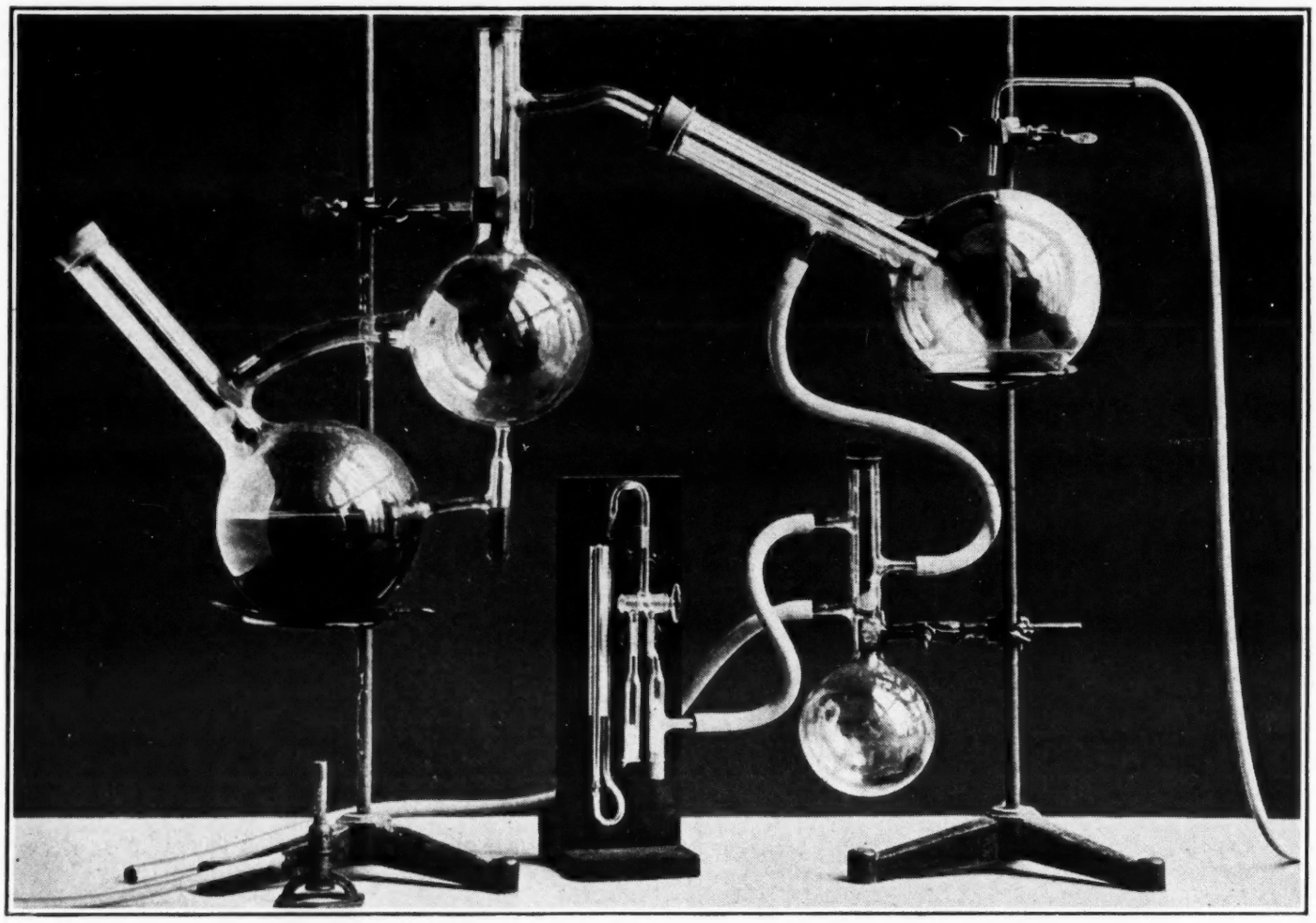
A Distillation Set-up for Frothing Liquids

OWING to the fact that we are now supplying phenylhydrazine in larger quantities than most of our organic chemicals, it has become necessary for us to design a special flask for its distillation. Some lots have the tendency to froth excessively in undergoing distillation and this would require constant attention if ordinary apparatus were used. Our original set-up has undergone several changes to accommodate this particular chemical. The photograph reproduced on this page shows the general design of the present arrangement which works very well. We believe that it will prove useful in distilling other liquids that froth under similar conditions.

The distilling flask is made from a three-liter, long-neck, pyrex flask, which is connected by means of a 28 mm. tube to a two-liter, long-neck flask. A trap is sealed into the bottom of the smaller flask and connected with a return tube to the distilling vessel. The remainder of the set-up is the usual condensing receiver attached to the vacuum pump via the safety trap and manometer.

Distillation is started as usual and when the froth reaches the reservoir flask, the bubbles expand and break. The liquid collects in the trap below and is returned to the boiling flask. It is sometimes necessary, at the beginning, to warm the second flask with a small flame, but as soon as the distillation gets under way, the additional heating can be discontinued. Little attention to the apparatus is necessary thereafter.

Occasionally in vacuum distillation, some of the liquid condensing on the surface near the outlet tube is carried over into the receiver by the velocity of the vapor. This "creeping" does not take place in the type of apparatus described since any liquid that reaches the reservoir is automatically returned to the distilling flask.



Eastman Organic Chemicals as Analytical Reagents

XVII. REAGENTS FOR SILVER

p–DIMETHYLAMINOBENZAL–RHODANINE

Kolthoff: J.A.C.S. *52*, 2222 (1930)

The reagent recommended by Feigl consists of a saturated solution of this compound in alcohol. With weakly acid, neutral, and ammoniacal solutions it gives a red precipitate with silver. In very dilute solutions a red or reddish-brown color is produced in silver concentrations as low as 0.5 mg. per liter. A similar reaction is noted with solutions of copper and mercury.

DICHLOROFLUORESCEIN

Kolthoff, Lauer and Sunde: J.A.C.S. *51*, 3273 (1929)

In the titration of chlorides with silver nitrate, Dichlorofluorescein used as an indicator determines the endpoint very accurately. The indicator consists of a solution of 0.1 g. Dichlorofluorescein and 2.5 cc. of 0.1 N sodium hydroxide made up to 100 cc. with distilled water. Just at the endpoint of the titration the precipitated silver chloride turns dark red, owing to the adsorption of silver ions and the formation of red silver fluoresceinate. (To titrate a silver nitrate solution, a known amount of sodium chloride solution is added and the excess titrated with a standard silver nitrate, using the indicator.)

CHROMOTROPIC ACID

Gutzeit, Helv. Chim. Acta *12*, 714 (1929)

Silver solutions give a black precipitate with chromotropic acid. Iron produces an intense green coloration which may be removed by acidifying or treating with stannous chloride. Mercury gives a yellow color, which is masked by that of the silver.

METHYLAMINE

Martini, Mikrochemie *7*, 233 (1929)

Silver can be detected microchemically by treating a drop of the solution under examination with a drop of acetic acid and a drop of methylamine solution. The crystals of silver methylamine acetate formed are easily distinguished from the lead and mercury compounds by their form.

New Eastman Organic Chemicals

The following chemicals have been added to our list since the last edition of this *Bulletin*. Over 2,700 items are now in stock.

*iso-Amyl Stearate (Practical)

*Benzyl Succinic Acid (Practical)

*Cinnamylacetophenone

*Dichlorofluorescein

*3.4–Dichloronitrobenzene

*p–Dimethylaminobenzalrhodanine

*Ethoxyethyl Adipate

*Indophenol (Technical)

*o–Iodophenetole

*p–Iodophenetole

*a–Methyl Choline Chloride

Naphthalene–1.5–disulfonic Acid (Technical)

Naphthalene–2.7–disulfonic Acid (Technical)

*sec.–Octyl Stearate (Practical)

N–Phenyl–β–naphthylamine (Practical)

*n–Propyl Phthalate

*Rhodanine

Tetraiodophenolsulfonphthalein

Tetraphenyltin

*Tri–m–cresyl Phosphate

**Made in our own laboratories at Kodak Park.*